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FLUORINATED ENETHIOLS*

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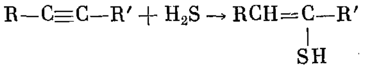
The closest analog of the well-studied keto—enol system is the enethiol—thione system. However, studies of prototropy in the latter system are extremely difficult [3-6] as a result of the instability of both forms, and their liability to undergo interconversion both in the presence of a variety of reagents, and also spontaneously, with the consequence that studies of this problem contain numerous contradictions and erroneous data [7].

The introduction of fluorine atoms and perfluoroalkyl groups usually confers high kinetic stability on unstable enols [8], and it was therefore to be expected that perfluorinated enethiols would be more stable, and hence more convenient for study.

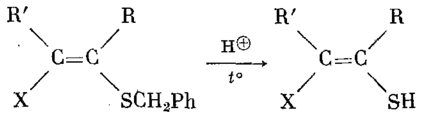
Perfluorinated enethiols have hitherto been unknown. Radical addition of H_2S to acetylenes [9] affords only hydrogen-containing analogs, which polymerize on storage. Their conversion into the corresponding thiocarbonyl compounds was not reported in [9].



$$R{-}C{\equiv}C{-}R' + H_2S \rightarrow RCH{=}\underset{\underset{\displaystyle SH}{|}}{C}{-}R'$$

$R = R' = CF_3$ (a) $R = CF_3$, $R' = H$ (b).

We have developed a general method for the preparation of perfluorinated enethiols of the aliphatic and alicyclic series which involves heating perfluoroalkenyl(cycloalkenyl) benzyl sulfides with fluorosulfuric or sulfuric acid, with the simultaneous removal of volatile products. Thus, enethiols (I)-(IV) affords the enethiols (V)-(VIII), which are stable compounds which remain unchanged on storage



(I)—(IV) (V)—(VIII)

$R = R' = CF_3$, $X = Cl$ (I), (V); $R, R' = -(-CF_2-)_2-$, $X = F$ (II), (VI); $R, R' = -(-CF_2-)_3-$, $X = CF_3$ (III), (VII); $R, R' = -(-CF_2-)_4-$, $X = Cl$ (IV), (VIII).

Acid hydrolysis of benzyl or tert-butyl perfluoro(1-ethyl-2-methyl-1-propenyl) sulfide (IXa, b) under similar conditions gives a mixture consisting of the enethiol (X) (86.3%) and

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*For previous communications, see [1, 2].

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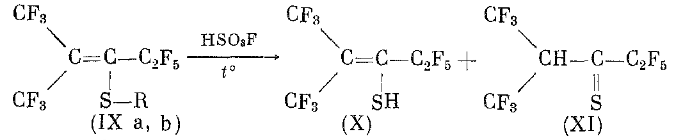
the corresponding thioketone (XI) (13.7%)

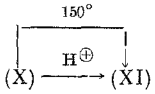


(IX a, b) (X) (XI)

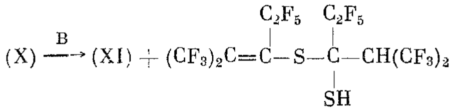
R = $PhCH_2$ (a), Me_3C (b).

This mixture is not in equilibrium. Distillation afforded the pure enethiol (X), which is a colorless compound, stable on keeping.

The enethiol (X) was converted into the thioketone (XI) by heating in a glass ampul for 20 h at 150°C, and by treatment with acids (boiling for 40 min in the presence of HSO_3F) or weak bases (Et_2O, $Et_3N \cdot BF_3$). The thioketone (XI) is a stable, deep blue compound



In the reaction involving proton transfer catalyzed by bases, in addition to (XI) the adduct (XII) was isolated. This was formed by addition of the enethiol form (X) to the thioketone (XI)

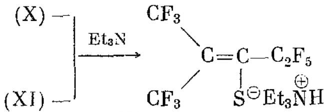


$$(X) \xrightarrow{B} (XI) + (CF_3)_2C{=}\overset{C_2F_5}{C}{-}S{-}\underset{SH}{\overset{C_2F_5}{C}}{-}CH(CF_3)_2$$

(XII)

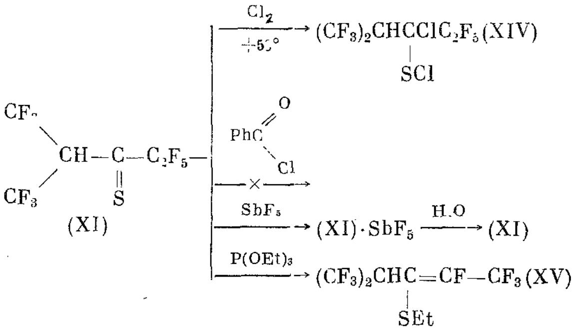
B = Et_2O; $Et_3N \cdot BE_3$.

The powerful base Et_3N detaches a proton from both forms to give the triethylammonium salt (XIII), which according to ^{19}F NMR has the enethiol structure



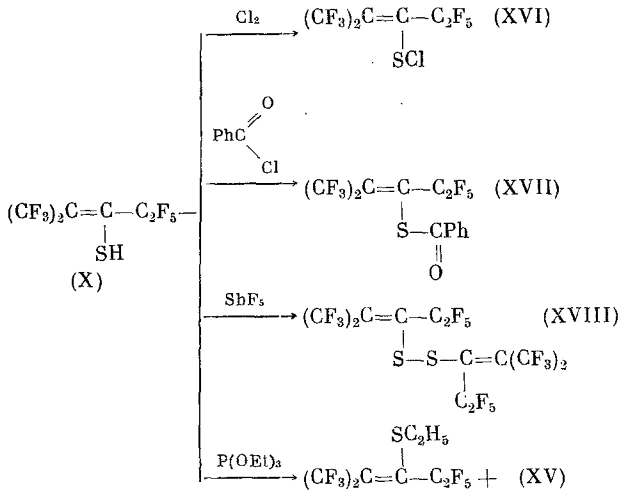
(XIII)

With the exception of the abovementioned reaction, the enethiol (X) and the thioketone (XI) differ sharply in their reactivities. Thus, the thioketone (XI) readily adds chlorine at the C=S double bond, does not react with benzoyl chloride at temperatures up to 160°C, reacts with SbF_5 to give a bright-yellow complex which on hydrolysis affords the original thioketone (XI), and reacts with triethyl phosphite like its oxygen analogs [10] to give the sulfide (XV)

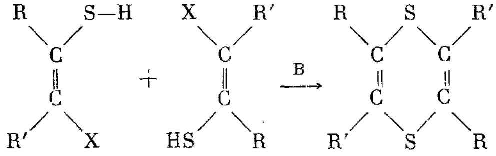


In contrast, the enethiol (X) undergoes chlorination to give the unsaturated sulfenyl chloride (XVI), on heating with benzoyl chloride it is benzoylated at the S atom, is oxidized by SbF_5 to the corresponding disulfide (XVIII), and gives with triethyl phosphite a mixture of sulfides (XIX) (68%) and (XV) (32%) (see Scheme at top of next page).

The formation of (XV) is readily explained in terms of the basic properties of triethyl phosphite, which causes partial isomerization of the enethiol (X) to the thioketone (XI), and reacts with the latter, as already noted, to give the sulfide (XV). These results show that perfluorinated enethiols are not in tautomeric equilibrium with the corresponding thioketones.



The irreversible isomerization of the enethiol (X) to the thioketone (XI) shows that the latter has the greatest thermodynamic stability. Enethiols (V), (VI), and (VIII), which carry a halogen atom at the double bond, could not be converted into the thioketones. These compounds are stable to acids, and on treatment with basic reagents they undergo cyclization to p-dithiines as a result of a competitive nucleophilic replacement reaction



(V), (VI), (VIII) (XX), (XXI), (XXII)

B = Et_2O, N-methylpyrrolidone; R = R′ = CF_3, X = Cl (V), (XX); R, R′ = $-(-CF_2-)_2-$, X = F (VI), (XXI); R, R′ = $-(-CF_2-)_4-$, X = Cl (VIII), (XXII).

Sulfides (I)-(IV) and (IX) were obtained by reaction of benzyl mercaptan with the corresponding olefins in the presence of Et_3N.

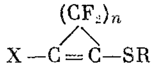
EXPERIMENTAL

^{19}F NMR and ^1H spectra were recorded on a Perkin–Elmer R-32 spectrometer (84.6 and 90 MHz, respectively), from the external standards CF_3CO_2H and TMS. IR spectra were obtained on a UR-20 spectrophotometer, and Raman spectra on a Ramanor HG-2S instrument, excitation being provided by the 5145 Å line of a CR-8 laser, power 100 mW. The UV spectrum was recorded on a Hitachi instrument. The purity of the compounds was checked by GLC on a LKhM-8MD apparatus (model 3), column with 20% QF on Chromaton. Mass spectra were obtained on a Varian MAT CH-8 apparatus (ionizing electron energy 70 eV), m/z and suggested assignments being given. For the purification of compounds by preparative GLC, a Perkin–Elmer F-21 instrument was used. Column 5 m × 20 mm, 20% QF on Chromaton. The ^{19}F NMR spectra of (II)-(VIII) are given in Table 1, and of (IX), (X), (XII), (XIII), and (XVI)-(XIX) in Table 2.

1-Benzylthio-3-chloroperfluoro-2-butene (I). To a solution of 15.1 g of 2-chloroperfluoro-2-butene [11] in 150 ml of dry ether, cooled to 0°C, was added slowly with stirring a mixture of 8.7 g of benzyl mercaptan and 7.1 g of Et_3N. The reaction mixture was kept for 1 h at 0°C, warmed to 10°C, and poured into water. The organic layer was separated, dried over $MgSO_4$, and distilled to give 11.9 g (53%) of (I), bp 60-72°C (1 mm). Found: C 41.48; H 2.30; F 36.06; S 9.68%. $C_{11}H_7ClF_6S$. Calculated: C 41.20; H 2.20; F 35.55; S 9.999%. ^{19}F NMR spectrum (δ, ppm, J, Hz): −20.9 q (CF_3^1); −17.8 q (CF_3^2); $J_{CF_3^1-CF_3^2}$ = 13.2 (cis-isomer); −18.2 m (CF_3^1); −17.1 m (CF_3^2); $J_{CF_3^1-CF_3^2} < 1.8$ (trans isomer).

1-Benzylthioperfluoro-1-cyclobutene (II). To a solution of 27.2 g of perfluorocyclobutene in 150 ml of ether was added with stirring (−3 to −5°C), dropwise, a mixture of 19.1 g of benzyl mercaptan and 15.9 g of Et_3N. The mixture was warmed to ~20°C, washed with water, and the ether layer dried over $MgSO_4$ and distilled to give 20.5 g (41.0%) of (II), bp 78°C (2 mm). Found: C 49.53; H 2.65; F 35.54; S 11.87%. $C_{11}H_7F_5S$. Calculated: C 49.62; H 2.63; F 35.71; S 12.03%. PMR spectrum (δ, ppm): 3.7 s (CH_2), 6.9 s (Ph). IR spectrum (ν, cm^{-1}): 1678 (C=C).

TABLE 1. ^{19}F NMR Spectra of Compounds with the General Formula (δ, ppm; J, Hz)



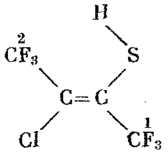
Compound	n	R	X	δCF_2^1	δCF_2^2	δCF_2^3	δCF_2^4	δX
(II)	2	$PhCH_2$	F	36,6 m	38,0 m	–	–	41,4 t.t *
(VI)	2	H	F	36,6 m	41,4 m	–	–	41,4 m
(III)	3	$PhCH_2$	CF_3	29,8 m	31,2 m	53,0 m	–	–16,7 m
(VII)	3	H	CF_3	32,9 m	37,1 m	54,6 m	–	–15,9 m
(IV)	4	$PhCH_2$	Cl	29,2 m	58,9 m	58,9 m	33,1 m	
(VIII)	4	H	Cl	29,1 m	56,2 m	56,2 m	31,3 m	

*$J_{CF_2^1-F}$ = 18.8; $F_{CF_2^2-F}$ = 6.6.

1-Benzylthioperfluoro-2-methyl-1-cyclopentene (III). To a mixture of 36.3 g of perfluoro-1-methyl-1-cyclopentene and 20.0 g of benzyl mercaptan in ether (150 ml) was added slowly 16.3 g of Et_3N, keeping the temperature at 20-25°C. The mixture was stirred for a further 2 h, washed with water, dried over $MgSO_4$, and distilled to give 35.0 g (59.5%) of (III), bp 95-97°C (2 mm). Found: C 42.63; H 1.81; F 46.27; S 8.94%. $C_{13}H_7F_9S$. Calculated: C 42.63; H 1.92; F 46.68; S 8.75%.

1-Benzylthio-2-chloroperfluoro-1-cyclohexene (IV). a) A mixture of 22.3 g of 1,2-dichloroperfluoro-1-cyclohexene, 7.7 g of Et_3N, and 130 ml of dry ether was cooled to 0°C, and 9.7 g of benzyl mercaptan was added slowly with stirring under argon. The mixture was stirred for a further 1 h at 0°C, and kept for 15 h at ∼20°C. The mixture was then poured into water, extracted with ether, the ether extracts dried over $MgSO_4$, and distilled to give 11.2 g (38.7%) of (IV), bp 90-93°C (0.5 mm). Found: C 40.83; H 1.86; F 39.75; S 8.15%. $C_{13}H_7ClF_8S$. Calculated: C 40.80; H 1.84; F 39.72; S 8.38%. PMR spectrum (δ, ppm): 4.0 s (CH_2), 7.1 s (Ph).

b) To 6.9 g of 1-chloroperfluoro-1-cyclohexene, 2.5 g of Et_3N, and 60 ml of dry ether was added slowly under argon at 20°C 3.1 g of benzyl mercaptan. The mixture was stirred for 1 h, and worked up as in the preceding example to give 5.5 g (57.8%) of (IV).

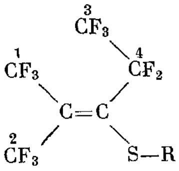
3-Chloroperfluoro-2-butene-2-thiol (V). To 6.8 g of (I) in a distillation apparatus was added slowly from a dropping funnel 4 ml of freshly distilled HSO_3F. The mixture was heated with the flame of a burner, and the fraction boiling up to 110°C was collected. This was distilled repeatedly to give 1.6 g (32.7%) of (V), bp 73-93°C. Found: C 20.27; H 0.51; F 49.11; S 13.54%. C_4HClF_6S. Calculated: C 20.84; H 0.44; F 49.44; S 13.91%. Raman spectrum (ν, cm^{-1}) 1590 (C=C), 2592, 2612 (SH of the cis and trans isomers . ^{19}F NMR spectrum (δ, ppm, J, Hz) –15.1 m (CF_3^1), –14.7 d.q. (CF_3^2) $J_{CF_3^1-CF_3^2}$ = 1.8; $J_{CF_3^2-H}$ = 5.4 (trans-isomers): –20.0 q (CF_3^1), –17.3 q (CF_3^2), $J_{CF_3^1-CF_3^2}$ = 13.2 (cis isomer). PMR spectrum (δ, ppm, J, Hz): 3.8 q (SH), $J_{H-CF_3^2}$ = 5 (trans isomer), 4.1 s (SH) (cis-isomer).

Perfluoro-1-cyclobutene-1-thiol (VI). In a distillation apparatus were placed 4.4 g of (II) and 1 ml of freshly distilled HSO_3F. The mixture was heated with the flame of a burner, and the fraction boiling up to 80°C was collected in an ice-cooled receiver. Repeated distillation gave 0.76 g (28.8%) of (VI), bp 70-71°C. Found: C 27.16; H 0.57; F 53.52; S 18.13%. C_4HF_5S. Calculated: C 27.28; H 0.575; F 53.94; S 18.20%. IR spectrum (ν, cm^{-1}): 1695 (C=C); 2590 (SH). PMR spectrum (δ, ppm): 3.6 s (SH).

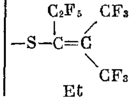
Perfluoro-2-methyl-1-cyclopentene-1-thiol (VII). In a distillation apparatus were placed 5.7 g of (III) and 3.6 ml of conc. H_2SO_4. The mixture was heated with the flame of a burner, and the fraction boiling up to 120°C was collected. This was repeatedly distilled from its mixture with 3 ml of conc. H_2SO_4 to give 2.0 g (46.5%) of (VII), bp 100-101°C. Found: F 62.33; S 11.67%. C_6HF_9S. Calculated: F 61.93; S 11.61%. IR spectrum (ν, cm^{-1}): 1635 (C=C), 2600 (SH). PMR spectrum (δ, ppm): 3.6 m (SH).

2-Chloroperfluoro-1-cyclohexene-1-thiol (VIII). In a distillation apparatus were placed 4.3 g of (IV) and 1.8 ml of conc. H_2SO_4. The mixture was heated with the flame of a burner,

TABLE 2. ^{19}F NMR Spectra of Compounds with the General Formula



(δ, ppm; J, Hz)

Compound	R	δ_1	δ_2	δ_3	δ_4	J_{1-2}	J_{1-3}	J_{1-4}
(IXa)	$PhCH_2$	−20,6 t.q.q	−17,3 q	−0,4 q	25,8 q	9,4	9,0	18.8
(IXb)	Me_3C	−20,0 m	−20,0m	−0,7 q	24,9 q	–	7,5	20,7
(X)	H	−20,6 t.q.q.	−17,3q.d	1,8q	26,9 q	11,3	9,5	22,6
(XIII)	$H\overset{\oplus}{N}Et_3$	−26,4 t.q.q.	−20,2 q	−1,8q	22,4 q	9,4	5,6	18,8
(XVI)	Cl	−19,1 "	−17,0 q	0,4q	25,6 q	9,4	9,4	18,8
(XVII)	PhCO	−20,1 "	−16,9 q	1,0q	26,4 q	11,3	9,4	21,6
(XVIII)	 $-S-C(C_2F_5)=C(CF_3)_2$	−19,1 m	−19,1 m	1,3 q	25,6 q	9,4	9,4	20,7
(XIX)	Et	−20,0 t.q.q.	−16,2 q	0 q	26,2 q	9,4	9,4	17,9

and the fraction boiling up to 145°C was collected. To this was added 1.5 ml of H_2SO_4, and redistilled to give 2.2 g (66.3%) of (VIII), bp 134-137°C. The analytical sample was distilled once more. Found: C 24.81; H 0.36; F 51.85; S 10.80%. C_6HClF_8S. Calculated: C 24.63; H 0.34; F 51.95; S 10.96%. IR spectrum (ν, cm^{-1}): 1610 (C=C), 2605 (SH). PMR spectrum (δ, ppm): 3.9 (SH).

2-Trifluoromethyl-3-benzylthio-perfluoro-2-pentene (IXa). To a mixture of 17.9 g of perfluoro-2-methyl-2-pentene, 7.4 g of benzyl mercaptan, and 70 ml of dry ether, cooled to 0°C was added slowly with stirring 6.0 g of Et_3N, maintaining the temperature at 0°C. After this the mixture was poured into water, extracted with ether, and the ether extract was dried over $MgSO_4$ and distilled. There was obtained 16.0 g (65%) of (IXa), bp 72-75°C (2 mm) (cf. [12]).

2-Trifluoromethyl-3-tert-butylthioperfluoro-2-pentene (IXb). A mixture of 5.1 g of perfluoro-2-methyl-2-pentene, 1.6 g of tert-butyl mercaptan, 1.8 g of Et_3N, and 50 ml of dry ether was boiled for 4 h, then poured into water, the ether layer separated, dried over $MgSO_4$, and distilled to give 4.3 g (68.0%) of (IXb), bp 74°C (40 mm). Found: C 32.24; H 2.30; F 55.89; S 8.69%. $C_{10}H_9F_{11}S$. Calculated: C 32.43; H 2.43; F 56.48; S 8.64%. IR spectrum (ν, cm^{-1}): 1585 (C=C). PMR spectrum (δ, ppm); 1.3 s (Me).

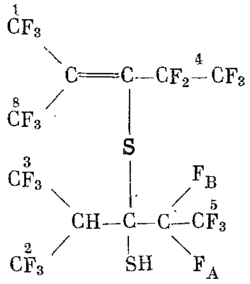
Perfluoro-2-methyl-2-pentene-3-thiol (X). a) In a distillation apparatus were placed 5.0 g of (IXa) and 4.0 ml of freshly distilled HSO_3F. The mixture was heated with the flame of a burner, and the fraction boiling up to 110°C was collected. A further distillation gave 3.2 g (82.2%) of a mixture bp 92-100°C, containing 86.3% of (X) and 13.7% of (XI). Redistillation gave (X), bp 101-102°C. Found: F 66.56; S 10.32%. $C_6HF_{11}S$. Calculated: F 66.53; S 10.21%. IR spectrum (ν, cm^{-1}): 1590 (C=C), 2640 (SH). PMR spectrum (δ, ppm): 3.9 q (SH).

b) Obtained similarly, but by heating the reaction mixture under vacuum (80 mm), 6.7 g of (IXa) and 4.0 ml of freshly distilled HSO_3F afforded 3.7 g (70.5%) of nearly pure (X), bp 52-53°C (120 mm).

c) As in b), 2.0 g of (IXb) and 1 ml of freshly distilled HSO_3F under a vacuum of 115 mm gave 1.6 g (93%) of a mixture containing 88% of (X) and 12% of (XI).

Reaction of (X) with Et_2O, $BF_3 \cdot NEt_3$, and HSO_3F. a) To 8.0 g of (X) was added 0.2 ml of dry ether, the mixture kept for 2 h, and 10 ml of conc. H_2SO_4 added. The mixture was then distilled to give 5.2 g (65.2%) of (XI), bp 80-81°C and 2.6 g (31.8%) of the adduct (XII), bp 79°C (10 mm). (XI): Found: C 22.86; H 0.20; F 66.41; S 10.25. $C_6HF_{11}S$. Calculated: C 22.94; H 0.32; F 66.53; S 10.21%. IR spectrum (ν, cm^{-1}): 2994 (CH). ^{19}F NMR spectrum (δ, ppm): −12.0 m [$(CF_3)_2$], 4.9 m (CF_3), 35.4 m (CF_2). PMR spectrum (δ, ppm; J, Hz): 4.8 hept (CH), $J_{(CF_3)_2-H} = 7.0$. UV spectrum (in hexane): λ_{max} 220; 305; 610 nm; ε_{220} 4857; ε_{305} 36; ε_{610} 6. (XII): Found: C 23.07; H 0.25; F 66.81; S 10.14%. $C_{12}H_2F_{22}S_2$. Calculated: C 22.94; H 0.32; F 66.53; S 10.21%. IR spectrum (ν, cm^{-1}): 1610 (C=C), 3000 (CH) (see Scheme at top of next page).

b) To 2.8 g of (X) was added 1.6 g of $BF_3 \cdot NEt_3$. When the slightly exothermic reaction was complete, the product was transferred in a 5 mm vacuum to a trap cooled at −78°C. There was obtained 1.6 g (58.0%) of (XI), bp 80-81°C.



^{19}F NMR spectrum (δ, ppm; J, Hz): −19.3 m (CF_3^1, CF_3^8); −17.6 q.d.d.d. (CF_3^2); −10.0 q.d. (CF_3^3); 1.3 q (CF_3^1); 4.2 s (CF_3^5); 24.5 q (CF_2); 36.0 (F_A); 37.8 (F_B); $J_{CF_3^1-CF_2}$ = 19.7, $J_{CF_3^1-CF_3^4}$ = $J_{CF_3^1-CF_3^8}$ = 9.4, $J_{CF_3^3-CF_3^2}$ = $J_{CF_3^2-F_A}$ = $J_{CF_3^2-F_B}$ = 9.4, $J_{F_A-F_B}$ = 276. PMR spectrum (δ, ppm): 3.9 t (SH), 3.4 hept (CH), $J_{CH-CF_3^2}$ = $J_{CH-CF_3^3}$ = 7.6, J_{H-F_A} = J_{H-F_B} = 14.0 Hz.

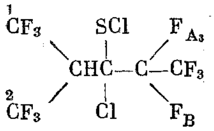
c) The enethiol (X) was heated with freshly distilled HSO_3F in a flask under reflux. According to ^{19}F NMR, after 40 min the (X) had been completely converted into the thioketone (XI).

d) Heating (X) in a glass ampul for 20 h at 150°C gave a quantitative yield of the thioketone (XI) (according to ^{19}F NMR).

Triethylammonium Enethiolate of Perfluoro-2-methyl-2-pentene-3-thiol (XIII). a) To 2.5 ml of dry Et_3N at −78°C was added dropwise 1.1 g of (X), the mixture warmed to ∼20°C, and excess Et_3N removed in vacuo (4 mm). According to NMR, the residue (1.4 g, 91.5%) consisted of pure (XIII). PMR spectrum (δ, ppm; J, Hz): 1.2 t (Me), 2.9 q (CH_2), 12.8 br.s. (H), J_{Me-CH_2} = 7.0.

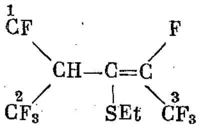
b) Similarly, from 1.5 ml of dry Et_3N and 0.4 g of (XI) there was obtained 0.6 g (99.9%) of (XIII).

2-Trifluoromethyl-2-hydro-3-chloroperfluoropentane-3-sulfenyl Chloride (XIV). In a steel autoclave were placed 3.1 g of (XI) and 3 ml of liquid Cl_2, and the mixture heated for 6 h at 50°C. Excess chlorine was then removed into a trap cooled to −78°C, and the residue was distilled to give 2.7 g (71.0%) of (XIV), bp 75-76°C (47 mm). Found: C 18.58; H 0.20; F 53.86; S 7.89%. $C_6HCl_2F_{11}S$. Calculated: C 18.72; H 0.26; F 54.28; S 8.33%. ^{19}F NMR (δ, ppm; J, Hz): −20.1 m.



(CF_3^1); −18.7 d.d q.d (CF_3^2); −2.2 s (CF_3^3); 22.2 (F_A); 31.1 (F_B); $J_{CF_3^2-F_A}$ = 26.3, $J_{CF_3^2-F_B}$ = 17.9, $J_{CF_3^2-CF_3^1}$ = 14.1, $J_{CF_3^2-H}$ = 7, $J_{F_A-F_B}$ = 280. PMR spectrum (δ, ppm; J, Hz): 4.2 hept (CH), $J_{CF_3^1-H}$ = $J_{CF_3^2-H}$ = 7.

3-Ethylthio-4-hydroperfluoro-4-methyl-2-pentene (XV). To 3.5 g of (XI), cooled to −78°C, was added dropwise 1.8 g of $P(OEt)_3$, the reaction mixture being periodically shaken. The mixture was then warmed to ∼20°C, and gradually heated to 40°C, volatile products being removed under a vacuum of 2 mm to a trap cooled to −78°C. There was obtained 2.3 g of material containing (by GLC) 90% of (XV), bp 127-130°C. Found: C 28.83; H 1.79; F 58.8; S 10.21%. $C_8H_6F_{10}S$. Calculated: C 29.63; H 1.87; F 58.61; S 9.89%. IR spectrum (ν, cm^{-1}): 1650 (C=C).



^{19}F NMR spectrum (δ, ppm; J, Hz): −13.3 d.m (CF_3^1, CF_3^2), −12.7 d.m. (CF_3^3), 24.0 q.m (F), $J_{CF_3^1, CF_3^2-H}$ = $J_{F-CF_3^3}$ = 7.5. PMR spectrum (δ, ppm): 1.1 t (Me), 2.8 q (CH_2), 4.2 hept. m. (CH).

Complex of (XI) with SbF_5. To 5 ml of SbF_5 was added slowly with shaking in a flask 2.9 g of (XI), whereupon the thioketone (XI) was decolorized. The reaction mixture was bright yellow in color, and contained no volatile products, since none were removed under a vacuum of 1 mm at ∿20°C. The mixture was poured into icewater, and the deep blue organic layer separated, dried over $MgSO_4$, and distilled to give 1.5 g (51.0%) of (XI).

Perfluoro-2-methyl-2-pentene-3-sulfenyl Chloride (XVI). Chlorine was passed through 2.3 g of (X), maintaining the temperature at ∿20°C. Distillation afforded 1.8 g (72.0%) of (XVI), bp 67-68°C (120 mm). Found: C 20.74; F 59.99; S 9.12%. $C_6ClF_{11}S$. Calculated: C 20.67; F 59.96; S 9.197%. IR spectrum (ν, cm^{-1}): 1600 (C=C).

2-Trifluoromethyl-3-benzoylthioperfluoro-2-pentene (XVII). A mixture of 3.0 g of (X) and 1.3 g of benzoyl chloride was heated for 20 h at 120°C, then distilled to give 0.7 g of (XI), bp 80-81°C, and 0.9 g (30%) of (XVII), bp 110-111°C (8 mm). Found: C 37.67, H 1.13; F 49.84%. $C_{13}H_5F_{11}OS$. Calculated: C 37.33; H 1.20; F 49.97%. IR spectrum (ν, cm^{-1}): 1590, 1600 (C=C, Ph), 1710 (C=O). PMR spectrum (δ, ppm): 7.2 m (Ph).

Di(Perfluoro-1-ethyl-2-methyl-1-propenyl) Disulfide (XVIII). To 13.4 g of SbF_5, cooled to 10°C, was added dropwise, slowly, with stirring, 2.2 g of (X). The reaction mixture was warmed to ∿20°C, poured into icewater, the organic layer separated, dried over $MgSO_4$, and distilled to give 0.8 g (36.5%) of (XVIII), bp 74-76°C (8 mm). Found: C 23.07; F 67.11; S 10.20%. $C_{12}F_{22}S_2$. Calculated: C 23.01; F 66.75; S 10.24%. IR spectrum (ν, cm^{-1}): 1600 (C=C).

2-Trifluoromethyl-3-ethylthioperfluoro-2-pentene (XIX) and (XV). As for (XV), from 0.7 g of $(EtO)_3P$ and 1.3 g of (X) there was obtained 1.0 g of a mixture containing (GLC and ^{19}F NMR) 68% of (XIX) and 32% of (XV), bp 127-140°C.

2,3,5,6-Tetrakis(trifluoromethyl)-p-dithiine (XX). To 10 ml of N-methylpyrrolidone, cooled to −78°C, was added dropwise 8.9 g of (V). The mixture was warmed to ∿20°C, poured into water, the organic layer separated, ether added, dried over $MgSO_4$, and distilled, the fraction bp 37-55°C (18 mm) being collected. The resulting mixture (3.3 g) contained (GLC and ^{19}F NMR) 82% of (XX). The analytical sample was purified by preparative GLC, bp 54-55°C (25 mm), mp 24-25°C, ^{19}F NMR spectrum in accordance with that reported [13]. Raman spectrum (ν, cm^{-1}): 1618 (C=C).

Octafluoro-2,7-dithiatricyclo[6.2.0.0^{3,6}]deca-1(8),3(6)-diene (XXI). A mixture of 0.6 g of (VI) and 2 ml of dry ether was kept for 24 h, and the ether was then removed to give 0.31 g (58%) of (XXI), mp 131-133°C (from ether–hexane). IR and ^{19}F NMR spectra as previously reported [14].

Perfluoro-1,2,3,4,6,7,8,9-octahydrothianthrene (XXII). a) To 2 ml of N-methylpyrrolidone was added slowly with cooling at 20°C 1.7 g of (VIII). The mixture was then poured into water, and the solid filtered off and recrystallized from methanol to give 0.7 g (46.4%) of (XXII), mp 88-90°C. Found: C 27.98; F 59.64; S 12.07%; mol. wt. 511.9800 (mass spectrum). $C_{12}F_{16}S_2$. Calculated: C 28.13; F 59.34; S 12.52%; mol. wt. 511.69186. IR spectrum (ν, cm^{-1}): 1600 (C=C).

b) Compound (XXII) was obtained similarly from (VIII) in DMFA, and it was also the main product of the reaction of (VIII) with EtOH (with heating), according to ^{19}F NMR and GLC.

CONCLUSIONS

1. A method has been found for the preparation of fluorinated enethiols by heating perfluoroalkenyl (or cycloalkenyl) benzyl sulfides with inorganic acids.

2. The enethiol form has been converted into the thiocarbonyl form, and the reactivities of both forms have been studied.

3. The perfluorinated enethiols are not in tautomeric equilibrium with the corresponding thioketones.

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GEMINAL SYSTEMS.

COMMUNICATION 20.* STRUCTURE AND PROPERTIES OF AMINOMETHYLPHOSPHONIUM SALTS

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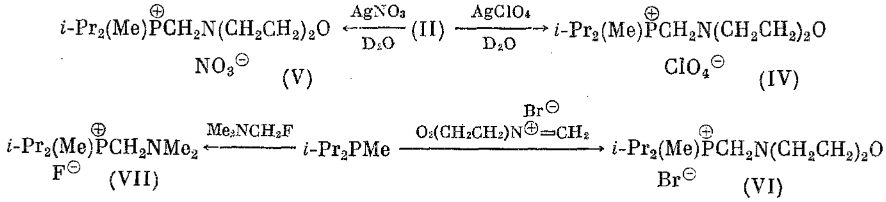
The phosphonium form of the phosphorus has greatest configurational stability [2]. Thus, for example, the PMR spectra of salts $[i\text{-Pr}(PhCH_2)Me\overset{\oplus}{P}H]\,I^{\ominus}$ [1] and $[i\text{-Pr}_2(PhCH_2)\,\overset{\oplus}{P}Me]Br^{\ominus}$ (I) show nonequivalence of the methyl group protons of the isopropyl substituent (eight signals instead of four).

The properties of aminomethylphosphonium salts (AMPS) were attributed in our previous work to an anomalous reduction in the configurational stability of the phosphorus atom for the following reasons [3, 4]. First, the PMR spectra of all prepared AMPS do not display the expected nonequivalence of the geminal protons and substituent groups at the phosphorus atom [1]. For example, Fig. 1 shows the equivalence of all three indicator groups (i-Pr, $CH_2N<$, and CH_2Ph). Second, this spectrum lacks the additional multiplicity of the morpholine ring CH_2N signal which arises in the spectrum of the original aminomethylphosphine [1] due to asymmetric indication of the chiral phosphorus atom. These effects are retained in different solvents such as $CDCl_3$ (see Fig. 1) taken instead of CD_3OD, in which a low value is found for $\Delta\nu$ of the methyl groups in $Me_2\overset{\oplus}{P}(Ph)CH(Ph)Me\ \overset{\ominus}{Br}$ [5]. In the PMR spectrum of $[i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N-(CH_2CH_2)_2O]\,I^{\ominus}$ (II) in Freon-21, the signals of the indicator groups are not split even upon cooling to –100°C, and the ^{13}C NMR spectrum shows equivalence of the methyl carbons and isopropyl groups in contrast to model phosphonium salt (III) (Table 1). The loss of the configurational stability of the phosphorus atom in AMPS may be attributed to the formation of a covalent P–anion bond and pseudorotation in the phosphorane formed. Since the question of the existence of iodophosphoranes is still not clear [6], we varied the $X^{\ominus}$ anions from those capable of forming a P–X bond to those to which formation of a covalent bond is very unlikely



$$\underset{NO_3^{\ominus}\quad (V)}{i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O} \xleftarrow[D_2O]{AgNO_3} (II) \xrightarrow[D_2O]{AgClO_4} \underset{ClO_4^{\ominus}\quad (IV)}{i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O}$$

$$\underset{F^{\ominus}\quad (VII)}{i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2NMe_2} \xleftarrow{Me_2NCH_2F} i\text{-Pr}_2PMe \xrightarrow{\overset{Br^{\ominus}}{O(CH_2CH_2)_2N^{\oplus}{=}CH_2}} \underset{Br^{\ominus}\quad (VI)}{i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O}$$

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*For Communication 19, see our previous work [1].

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